Prediction and Minimization of Vertical Migration of DNAPLs Using Surfactant Enhanced Aquifer Remediation at Neutral Buoyancy

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Abstract

Surfactant Enhanced Aquifer Remediation had previously been thought to require a capillary barrier below the contaminated zone to prevent the vertical migration of a microemulsion containing solubilized DNAPL. This paper shows the vertical migration of the dense microemulsion is described and predicted by the value of three dimensionless scaling groups. Embedded within these scaling groups are four design parameters. The value of these parameters can be

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manipulated in order to reduce the amount of vertical migration anticipated for a given remediation design. Plots have been constructed that illustrate the relationship between vertical migration and the value of the scaling groups; such plots can be used to predict vertical migration and to determine appropriate screen intervals of extraction wells to ensure full capture of the contaminants. This predictive capability has been verified in laboratory experiments. Predicted migration of the microemulsion agreed within about 2% of that observed. Development of the scaling groups is presented, remediation design implications are discussed, and laboratory verification is shown. Additional discussion of the laboratory work is given in a companion paper (Kostarelos et al., 1998).

Keywords

DNAPL, remediation, surfactants, vertical migration, buoyancy

1. Introduction

Remediation of water-bearing formations contaminated by organic liquids continues to be a challenge faced in both government facilities and manufacturing/industrial sites in the private sector. Because of their physical and chemical properties, chlorinated solvents such as trichloroethylene (TCE) are especially troublesome. Being more dense than the surrounding groundwater, mobile TCE will migrate below the water table, contaminating deeper water-bearing horizons. As a dense, nonaqueous phase liquid (DNAPL) migrates through the subsurface, a portion of the DNAPL is retained in the pore structures as discrete ganglia. This is typically referred to as a residual saturation of DNAPL, which can be as large as 40% of the pore volume (Wilson and Conrad, 1984). The principal method of DNAPL remediation currently in use is groundwater extraction coupled with above-ground treatment (i.e., "pump

and treat"). Mackay and Cherry (1989), however, have documented the limitations of this treatment method, and concluded that it can only be relied upon to contain groundwater contamination, not to actively remediate a contaminant source. The reason pump and treat is ineffective is the limited solubility of most DNAPL constituents in groundwater. Because of their low solubility, removal by groundwater extraction requires exceptionally long periods of time (Cohen and Mercer, 1993, p. 4-27).

Surfactant-enhanced aquifer remediation (SEAR) has received substantial attention in recent years as an emerging remediation technology (Ang and Abdul, 1991; West and Harwell, 1992; Pennell et al., 1994; Brown et al., 1994; Fountain et al., 1996; Martel and Gelinas, 1996). Surfactants increase the effective solubility of DNAPL compounds by orders of magnitude over their solubility in groundwater (Baran et al., 1994), thus accelerating the cleanup time and reducing its cost. SEAR was recently successfully demonstrated in a cleanup action at Hill Air Force Base (Brown et al., 1997). In that project, 99% of the DNAPL initially in place (which consisted primarily of TCE, PCE, and TCA) was recovered with approximately 2.5 pore volumes of chemical solution injected. The chemical mix used in this field experiment was an aqueous solution containing 8 wt% dihexyl-sulfosuccinate and 4 wt% IPA. The residual DNAPL saturation was reduced from about 0.04 to 0.0004 in the swept volume (about 60 m^3) of the unconfined, heterogeneous aquifer.

Despite the recent successes of SEAR, a perceived limitation of the method is the required presence of an aquitard below the DNAPL to reduce the risk of uncontrolled, vertical migration (Fountain et al., 1994). This perceived limitation

implies that no active remediation of DNAPL-contaminated sites can occur in aquifers not underlain by a capillary barrier to further vertical migration.

This paper describes a process whereby significant amounts of TCE may be solubilized in a microemulsion phase, such that the resulting phase density is at nearly neutral buoyancy with respect to the surrounding groundwater. A theoretical and numerical analysis demonstrates that vertical migration of a more dense phase (in this case, a microemulsion containing surfactant, alcohol, water, and TCE) can be predicted as a function of three dimensionless scaling groups. Within these scaling groups are four remediation design parameters; these parameters can be manipulated to reduce the relative importance of buoyancy and approach a neutral buoyancy displacement process. This extension of "conventional" SEAR - which we term SEAR-Neutral Buoyancy, or SEAR-NB - provides the capability for remediation in aquifers not underlain by a flow barrier. The ability to manipulate and predict the vertical migration of the microemulsion, developed from a theoretical and numerical approach, has been validated in a series of laboratory experiments.

A schematic of the SEAR-NB process is given in Figure 1.

2. Theory

The analysis is begun by writing the equations that describe the conservation of mass and momentum in a two-dimensional, vertical cross section of an aquifer (see Appendix A). These equations are then rewritten in dimensionless form through the use of inspectional analysis (Ruark, 1935). What were parameters in the original form of the equations become dimensionless scaling groups in the dimensionless equations. This approach provides solutions to the governing

equations that apply to all aquifers or model aquifers that are geometrically similar when the scaling groups and dimensionless variables are matched at the two scales. Thus, we are able to perform laboratory-scale (prototype) experiments in model aquifers and extrapolate the results to the field scale.

Prior to writing the governing equations in dimensionless form, certain assumptions were made regarding the displacement process. By doing so, we are essentially writing an incomplete set of governing equations, a method known as "partial inspectional analysis" (Birkhoff, 1950). This results only in the exclusion of specific phenomena (those demonstrated not important for our current purposes) from appearing in the dimensionless groups derived. An example of this is given in assumption 1 below: we neglect dispersion in the simplified governing equations. In doing so, we are assured of obtaining neither a longitudinal nor transverse dispersion number in our final set of dimensionless scaling groups; however, none of the other scaling groups are affected. The assumptions are used to simplify the process of inspectional analysis, though those regarding phase behavior of the chemical mixtures are also supported by laboratory studies (Kostarelos et al., 1998). The assumptions are discussed below.

1. Negligible dispersion in the transport; we are focusing only on "body forces" (i.e., viscous, gravity, and capillary forces). For the purposes of analyzing the vertical migration of dense contaminants, dispersion is a second-order effect that can be neglected without affecting the process.

2. Negligible adsorption of chemical species. Adsorption does in fact occur, but accounts for a very small fraction of the mass under the conditions of interest. In

fact, low adsorption of surfactant is one of the more important criteria in surfactant selection, since it has a direct bearing on cost of chemical.

3. No separation of injected surfactant and alcohol; i.e., transport occurs as a single chemical specie.

4. We neglect surfactant concentrations below the critical micelle concentration in the aqueous phase, the dissolution of contaminant in the aqueous phase, and dissolution of water in the DNAPL. We also assume Windsor type 1 phase behavior, and negligible chemical partitions into the DNAPL.

5. The DNAPL species are instantaneously solubilized when contacted by the injected chemical solution; thus the microemulsion density is assumed to be constant in time, and is only a function of surfactant, contaminant, alcohol, and water concentrations and densities. Mass transfer rates can be important in some situations; however, rapid solubilization is another important criteria used in surfactant selection (Dwarakanath, 1997). Furthermore, residence time is typically large compared to the time required to achieve equilibrium solubilization.

6. The interfacial tension between the DNAPL and microemulsion remains sufficiently large (more precisely, the trapping number is kept sufficiently small as per Jin, 1995 and Pennell et al., 1996) such that no mobilization of DNAPL occurs. Additional discussion of the trapping number can be found in the referenced literature.

7. Fluids and rock are assumed to be incompressible.

8. The medium is assumed to be homogeneous, but anisotropic.

When these assumptions are invoked, the governing equations take a simpler form. The simplified equations and inspectional analysis are given in Appendix A. Through this analysis, the transport of DNAPL species solubilized in a microemulsion is characterized by the following four dimensionless groups (see Nomenclature for definition of terms):

$$R_L = \frac{L}{H} \sqrt{\frac{k_z}{k_x}}$$
(1)

$$M^\circ = \frac{k_{r3}^o}{\mu_3} \frac{\mu_1}{k_{r1}^o}$$
(2)

$$N_G = \frac{\sqrt{k_x k_z} k_{r3}^o (\tilde{\rho}_3 - \tilde{\rho}_1) g}{\mu_3 u_T}$$
(3)

$$N_c = \frac{\mu_1 u_T}{k_{r1}^o k_x \sigma_{23}} \frac{L}{\sqrt{\varphi k_x}}$$
(4)

R_L, the effective aspect ratio (Zapata and Lake, 1981), can be thought of as a ratio of residence time of the injected fluid relative to vertical transit time. As R_L increases, there is more vertical flow, since the residence time is large relative to the transverse transit time.

The endpoint mobility ratio, M°, is the ratio of the endpoint mobility of the microemulsion (phase 3) divided by the endpoint mobility of the water (phase 1). The endpoint mobility of a phase is defined as the endpoint relative permeability divided by the viscosity. For an aqueous microemulsion, the relative permeabilities are nearly equal, so M° is approximately a ratio of the viscosities.

$M°$ may also be interpreted as a ratio of pressure gradients in the two phases. A mobility ratio less than one is favorable, since the injected fluid is less mobile than the groundwater, and therefore less likely to "finger" through the porous medium. Microemulsion mobility can be reduced (improving $M°$) by adding polymer to the chemical mixture, thereby increasing the viscosity.

The gravity number, N_G, is a ratio of two of the forces involved in the displacement: buoyancy because of density differences between the microemulsion and the groundwater, divided by viscous forces that arise from injection and extraction. A "large" value of N_G indicates that gravity forces are important, and the fluid is capable of significant vertical movement (i.e., gravity-driven flow); the opposite can be said for N_G "small." Specific values depend on the fluids and porous media under consideration. N_c is known as the capillary number, and is a ratio of the viscous driving forces divided by the capillary forces trapping the DNAPL. Sufficiently small N_c ensures that no mobilization of the DNAPL will occur. A microscopic analysis (Jin, 1995; Pennell et al., 1996) shows that a more precise requirement to ensure no mobilization of DNAPL is to maintain a sufficiently low trapping number, N_T. N_T is a generalization of the capillary number; however, it cannot be obtained from the continuum assumptions in the governing equations.   In the process described here (solubilization), N_c (or N_T) is intentionally kept sufficiently small (microemulsion/DNAPL interfacial tension kept sufficiently large) such that the DNAPL remains immobile, and N_c will therefore not be discussed further.

A summary of the scaling groups and their physical significance is given in Table 1. Inspectional analysis shows this displacement process is described by these dimensionless scaling groups. However, it does not indicate what the

relationship is between the value of these scaling groups and vertical migration of the microemulsion. In order to determine that relationship, a numerical study was conducted.

3. Numerical Studies

Numerical experiments were designed to identify the relationship between vertical migration and the value of the three scaling groups, $M°$, N_G, and R_L. The numerical simulator Tetrad (Vinsome and Shook, 1993) was used in this study. A two-dimensional grid was set up and a pressure gradient was established uniformly across the grid from left to right in order to establish flow. DNAPL was then introduced on the upper left side and allowed to flow across the domain. Because of the assumptions discussed in the theoretical development (most importantly, rapid solubilization and negligible dissolution of chemical in the aqueous phase), DNAPL displacing groundwater is a satisfactory proxy for a microemulsion displacing groundwater for the purposes of these simulations. Flow rates, fluid densities, horizontal and vertical permeabilities, interwell distances, endpoint relative permeabilities, and viscosities were all varied in order to evaluate the appropriate range of values of the scaling groups. A limited grid refinement study was also conducted, to assure sufficient accuracy in these results. For each simulation, four calculations or observations were required: the value of $M°$, N_G, and R_L, and the deepest vertical migration of the DNAPL, h. These were used to construct the crossplots discussed below.

The results of the numerical study are summarized in Figures 2a-c. In this figure, vertical migration of the DNAPL is plotted as a function of N_G and R_L for three different mobility ratios, $M°$. The values of $M°$ shown should not be taken as bounding values; rather, the process was simulated at a favorable ($M° = 0.5$),

an unfavorable (M° = 2.), and a unit mobility ratio. In these figures, observed vertical migration, h, has been normalized by overall thickness available for migration, H, in order to obtain a general expression for vertical migration. Furthermore, results of individual simulations have been replaced by a linear least squares curve fit over the entire range of simulated values. In all cases the correlation coefficient obtained was greater than 0.99.

Results shown in Figure 2 illustrate several points. First, at both favorable (M°=0.5) and unfavorable (M°=2) mobility ratios, viscous forces increase the vertical flow of the DNAPL at sufficiently large aspect ratios. For example, a relative vertical migration of h/H = 0.25 cannot be achieved at $R_L > 0.3$ for M° = 0.5 (Fig. 2a). Constraints on R_L are similar for unfavorable mobility ratios (Fig. 2c). This suggests physical limits on the remediation design. Relative vertical migration may in general be reduced, but at an increased cost (e.g., smaller well spacing reduces R_L and therefore vertical migration, but also means more wells).

It is worthwhile to note here that, while these crossplots are a useful means of predicting vertical migration during cleanup, they do not replace site-specific studies for field deployment. Careful laboratory and numerical analyses, using site soils and contaminants, must be performed to deploy any remediation technology with confidence. Site heterogeneity, for example, can have a profound influence on vertical migration of a more dense phase. Thus, while we believe that these plots have use as screening tools, a careful study using site specific data must be performed prior to field deployment of SEAR - or any other remediation process.

4. Implications for design: Minimization of vertical migration

While the ability to predict vertical migration of a DNAPL is of practical utility, through inspectional analysis we have shown the ability to manipulate the migration as well. Four design variables appear in the scaling groups derived (Eqns 1-4): microemulsion phase density,

Error!

Of the four design parameters, the only one which affects buoyancy *per se* is microemulsion phase density,

Error!

The crossplots given in Figure 2 can be used in a variety of ways. For example, one may determine the value of the scaling groups and predict vertical displacement of the microemulsion. One may also determine any three of the four design parameters, fix the "acceptable" vertical displacement (and ensure that wells are screened deeply enough for capture), and calculate the required value of the fourth design parameter. One would most frequently fix all but well spacing and determine the well spacing required, but fixing any three of the four results in the same process. For example, in the verification experiment discussed below, injection rate and microemulsion density were the variables manipulated in order to give a specified migration during the displacement. Experimental verification is summarized below; this experiment and others are discussed in detail in a companion paper in this issue (Kostarelos et al., 1998).

5. Experimental Verification

A laboratory experiment was performed to verify the predictive capabilities described above. In the experiment, a known amount of TCE was spilled into a

sand tank, solubilized by injected chemicals, and its vertical migration observed during the displacement. The tank has dimensions of 1.03 m in length, 0.41 m in height, and 0.051 m in thickness, approximating a vertical cross section of a model aquifer. After packing the tank with sand, it was filled with water, and conservative tracer tests were conducted to measure the pore volume and permeability. The water table was then lowered, a known amount of TCE (which was dyed to facilitate subsequent observations) was introduced, and the water table was again raised. Constant pressure was maintained at the extraction end of the tank, and chemicals were injected on the opposite end at a constant rate. The migration of the solubilized TCE was observed and plotted on the side of the tank throughout the test.

The surfactant used in these experiments is sodium dihexyl sulfosuccinate, which is a food-grade additive. Isopropyl alcohol (IPA) was the alcohol selected, primarily for its low density. Alcohol provides other benefits as well, including improved microemulsion phase behavior and enhanced compatibility between the surfactant and polymer. For this specific surfactant, however, the density is the most important characteristic of the alcohol. Xanthan gum, a biopolymer, was used for viscosity control. The injected chemical composition was an aqueous solution containing 4 wt% surfactant, 8 wt% IPA, 0.05 wt% polymer, and 0.4 wt% NaCl. This chemical composition results in a maximum solubility of TCE of approximately 3.3 wt% (33,000 mg/l). The resulting microemulsion phase density under these conditions is 1.003 g/cc (Kostarelos et al., 1998). Additional details of the phase behavior and suitability for TCE remediation is given by Dwarakanath et al. (1998).

Analysis of the conservative tracer tests indicated that the swept pore volume of the tank was 7,670 cm^3, and the horizontal permeability was 1.01×10^{-11} m^2 (10.2 D). For lack of measurement, vertical permeability was assumed to be equal to the horizontal permeability. 170 cm^3 of TCE was spilled near the center of the tank, and the distance between the "bottom" of the TCE residual and the bottom of the tank (H), and from the leading edge of the TCE to the extraction well (L) were measured. Partitioning tracer tests (Jin et al., 1995) indicated that the average TCE saturation was 2.2 vol%, which is consistent with the ratio of TCE spilled to pore volume. Figure 3 shows the initial condition for the experiment, with dimensions H and L marked.

The chemicals were injected along the entire left-hand side of the sand tank. The injection rate was selected such that the resulting volumetric flux was a constant 0.3 m/d. At this rate, the microemulsion had a viscosity of approximately 5 mPa-s (5 cp). Injection of such a viscous fluid caused the injection pressure to rise unacceptably. Due to these injection pressure increases, the injection rate was halved after 1.2 pore volumes had been injected. For reasons discussed below, this rate change had negligible effect on the vertical migration.

A TCE effluent history for this experiment is given in Figure 4. Also noted on this figure is the dimensionless time (pore volumes injected) at which the injection rate was reduced. Vertical velocity at the time the rate was changed is estimated from Darcy's law (using $\Delta \rho g$ as the pressure gradient) as 0.04 cm/hr, giving a maximum vertical migration of less that 2 cm over the next 50 hours (through $t_D = 2$; essentially through the end of significant solubilization). Furthermore, the rate change occurred after more than 1 pore volume was

injected, so the mobility ratio was approximately unity. One may therefore discount viscous crossflow, which would occur at small values of $M°$, R_L and N_G (see Figure 2a) from enhancing vertical migration. For these reasons, we believe the rate change has negligible effect on vertical displacement. This was further confirmed in a numerical simulation in which the rate change was explicitly accounted for.

Using the data (e.g., H, L, $\Delta\rho$, etc.) from this experiment, the values of the scaling groups can be calculated. The information used in the calculations is summarized in Table 2. The predicted relative vertical migration (h/H) is 0.833. Throughout the experiment, the migration of the solubilized TCE was plotted on the side of the tank. The deepest migration observed in this experiment was 82% of the overall distance available for migration (h/H = 0.82), thus confirming our ability to accurately predict migration under these conditions. Given the assumptions involved (e.g., $k_v = k_x$, L, H, and h estimated visually), such agreement is excellent. A photograph of the displacement at the approximate time of the change in injection rate is given in Figure 5. Post-flood partitioning tracer tests indicate that , within the accuracy of this method for estimating DNAPL saturation (± 0.001 DNAPL saturation under these conditions), complete removal of DNAPL was achieved.

6. Summary and Conclusions

This paper describes a means of predicting and manipulating the vertical migration of a microemulsion containing solubilized TCE to minimize buoyancy-driven flow. Through a theoretical analysis, we have shown that migration of the microemulsion is a function of three dimensionless scaling groups. Within these groups are four design parameters, all of which can be manipulated to minimize

the vertical migration. Through such manipulation, we are able to implement surfactant-enhanced aquifer remediation (SEAR) even in aquifers not underlain by a capillary barrier to vertical flow. We term this extension of the more conventional technology SEAR-Neutral Buoyancy, or SEAR-NB.

In addition to providing the means of manipulating the vertical migration, numerical studies have demonstrated that such migration may also be predicted as a function of those scaling groups. Plots such as those given in Figure 2 may be constructed for a given set of data and used to predict vertical migration; wells may then be screened to sufficient depth to ensure full capture of the contaminant. This capability, validated in laboratory experiments, removes undue concern over vertical migration of the contaminant, and provides the opportunity for cleanup of DNAPLs in environments previously not considered amenable to active cleanup efforts.

Despite the success of the predictions made on the laboratory experiments, we wish to emphasize the continued need for in-depth laboratory studies and numerical design simulations to successfully deploy SEAR-NB in the field. Such tools as presented in this paper, including both prediction and manipulation of the effects of buoyancy, have their use. Under no circumstances, however, should they be viewed as a replacement for careful, site-specific analysis and design.

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